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Approximation of Chronopotentiometric Responses
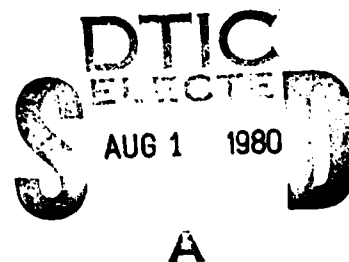by Orthogonal Collocation

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

High accuracy simulations of chronopotentiometric responses are demonstrated for several electrochemical mechanisms. Derivation of the discretized equations for simple electron transfer and EC mechanisms are given and others are tabulated.

Approximation of Chronopotentiometric Responses by Orthogonal Collocation

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Abstract

High accuracy simulations of chronopotentiometric responses are demonstrated for several electrochemical mechanisms. Derivation of the discretized equations for simple electron transfer and the EC mechanisms are given. The equations for other mechanisms are tabulated.

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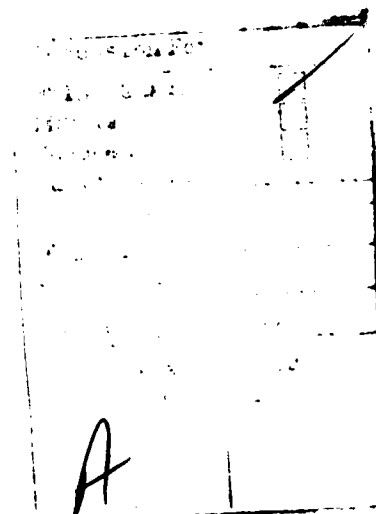
The advantages in using the orthogonal collocation technique for the simulation of second order partial differential equations describing electrochemical diffusion problems have been reported[1,2]. The discretized equations have been derived for several electrochemical mechanisms under the control of chronoamperometric[1-4] and cyclic voltammetric[5] programs. This paper presents the discretized equations necessary to simulate the chronopotentiometric response for two mechanisms. Extension of the technique to more complicated mechanistic schemes is shown to be straightforward, and the appendix contains further examples.

Symbol	Definition
[A]; [B]; etc.	Molar concentrations of species A, B, etc.
[A°]	Bulk concentration (initial) of species A
$A_{i,j}$; $B_{i,j}$	Discretization coefficients[1-5]
A	Electrode area, cm^2
β	$D\tau/z^2$
c_A; c_B; etc.	[A]/[A°]; [B]/[A°]; etc.
D_A; D_B; etc.	Diffusion coefficients of species A, B, etc.
D	$= D_A = D_B = D_C$, etc.
δ_{ij}	Kronecker delta (= 1 if i = j; = 0 if i $\neq$ j)
E	Potential
E°	Standard potential
F	Faraday
i	Current, amperes
J_{ij}	Elements of the Jacobian matrix
K	Homogeneous equilibrium constant
k	Homogeneous rate constant
n	Number of electrons transferred
N	Order of polynomial used

Symbol	Definition
R	Gas Constant
T'	Temperature
T	Time, seconds
τ	Chronopotentiometric transition time
t	$= T/\tau$
X	Perpendicular distance from electrode surface (cm)
x	X/Z
x_i	Roots of orthogonal polynomial (Legendre)
Z	Distance in solution from electrode surface where diffusional effects are negligible during time of experiment

Simple Reversible Charge Transfer

$$A \underset{}{\overset{ne^-}{\rightleftharpoons}} B \qquad (1)$$

This mechanism is considered for the planar diffusion case where initially only species A is present. At t = 0, a constant current i is applied to the cell, and the potential-time plot is recorded, noting the transition time τ. The response is given analytically by[6]

$$E = E^\circ - \frac{RT'}{nF} \ln \frac{T^{\frac{1}{2}}}{\tau^{\frac{1}{2}} - T^{\frac{1}{2}}} \qquad (2)$$

Although this solution is fully adequate for describing the response after corrections for charging, derivation of the discretized collocation equations will be given so as to exemplify the procedure that is followed for developing the approximation of the responses of more complicated mechanisms.

The diffusion equations and boundary conditions describing this experiment are

$$\frac{\delta [A]}{\delta T} = D_A \frac{\delta^2 [A]}{\delta x^2} \tag{3}$$

$$\frac{\delta [B]}{\delta T} = D_B \frac{\delta^2 [B]}{\delta x^2} \tag{4}$$

$$[A]_{x,0} = [A]_{\infty,t} = [A^\circ] \tag{5}$$

$$[B]_{x,0} = [B]_{\infty,t} = 0 \tag{6}$$

$$D = D_A \tag{7}$$

$$D = D_B \tag{8}$$

$$D_A \left(\frac{\delta [A]}{\delta X}\right)_{X=0} = -D_B \left(\frac{\delta [B]}{\delta X}\right)_{X=0} \tag{9}$$

$$i = nFAD_A \left(\frac{\delta [A]}{\delta X}\right)_{X=0} \tag{10}$$

$$E = E^\circ - \frac{RT'}{nF} \ln \frac{[B]_{X=0}}{[A]_{X=0}} \tag{11}$$

Insertion of the dimensionless variables for concentration, distance, and time into (3) and (4) gives

$$\frac{[A^\circ]\delta c_A}{\tau \, \delta t} = \frac{D[A^\circ]\delta^2 c_A}{z^2 \delta x^2} \tag{12}$$

$$\frac{[A^\circ]\delta c_B}{\tau \, \delta t} = \frac{D[A^\circ]\delta^2 c_B}{z^2 \delta x^2} \tag{13}$$

and after simplifying,

$$\frac{\delta c_A}{\delta t} = \beta \frac{\delta^2 c_A}{\delta x^2} \qquad (14)$$

$$\frac{\delta c_B}{\delta t} = \beta \frac{\delta^2 c_B}{\delta x^2} \qquad (15)$$

The boundary conditions (5)-(7) are treated similarly and become:

$$c_A(x,0) = 1 \qquad c_A(1,t) = 1 \qquad (16)$$

$$c_B(x,0) = 0 \qquad c_B(1,t) = 0 \qquad (17)$$

$$\left(\frac{\delta c_A}{\delta x}\right)_{x=0} = -\left(\frac{\delta c_B}{\delta x}\right)_{x_1=0} \qquad (18)$$

The discretization equations for first and second order ordinary differentials have been given previously[1], and are:

$$\frac{dy(x,t)}{dx}\bigg|_{x_i} = \sum_{j=1}^{N+2} A_{k,j}\, y(x_j,t) \qquad (19)$$

$$\frac{d^2y(x,t)}{dx^2}\bigg|_{x_i} = \sum_{j=1}^{N+2} B_{i,j}\, y(x_j,t) \qquad (20)$$

when evaluated at the roots x_i of an orthogonal polynomial. (See computational section.)

Application of (20) to (14) and (15) at the roots of a Legendre polynomial yield

$$\frac{dc_A}{dt}\Bigg|_{x_i} = \beta \sum_{j=1}^{N+2} B_{i,j} \, c_A(x_j,t) \tag{21}$$

$$\frac{dc_B}{dt}\Bigg|_{x_i} = \beta \sum_{j=1}^{N+2} B_{i,j} \, c_B(x_j,t) \tag{22}$$

Expanding (21) and (22) partially, we have

$$\frac{dc_A}{dt}\Bigg|_{x_i} = \beta [B_{i,1} c_A(0,t) + B_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} B_{i,j} c_A(x_j,t)] \tag{23}$$

$$\frac{dc_B}{dt}\Bigg|_{x_i} = \beta [B_{i,1} c_B(0,t) + B_{i,N+2} c_B(1,t) + \sum_{j=2}^{N+1} B_{i,j} c_B(x_j,t)] \tag{24}$$

Insertion of the boundary conditions (16) and (17) yields

$$\frac{dc_A}{dt}\Bigg|_{x_i} = \beta [B_{i,1} c_A(0,t) + B_{i,N+2} + \sum_{j=1}^{N+2} B_{i,j} c_A(x_j,t)] \tag{25}$$

$$\frac{dc_B}{dt}\Bigg|_{x_i} = \beta [B_{i,1} c_B(0,t) + \sum_{j=1}^{N+2} B_{i,j} c_B(x_j,t)] \tag{26}$$

We need an expression for $c_A(0,t)$ and $c_B(o,t)$ explicitly. From (20) applied to the boundary flux condition (18), we have

$$\frac{dc_A}{dx}\Bigg|_{x_1=0} = \sum_{j=1}^{N+2} A_{1,j} \, c_A(x_j,t) \tag{27}$$

$$\frac{dc_B}{dx}\Bigg|_{x_1=0} = \sum_{j=1}^{N+2} A_{1,j} \, c_B(x_j,t) \tag{28}$$

Now, equation (10) is also made dimensionless as follows. Since:

$$\left(\frac{d[A]}{dX}\right)_{x=0} = \frac{[A^\circ]}{L}\left(\frac{dc_A}{dx}\right)_{x_1=0} \quad , \quad \text{we have} \tag{29}$$

$$i = \frac{nFAD[A^\circ]}{L}\left(\frac{dc_A}{dx}\right)_{x_1=0} = \frac{nFA[A^\circ]D^{\frac{1}{2}}\beta^{\frac{1}{2}}}{\tau^{\frac{1}{2}}} \tag{30}$$

Combining this expression with (27) and (28), we have

$$c_A(0,t) = Q - \sum_{j=2}^{N+1} a_j c_A(x_j,t) \tag{31}$$

$$c_B(0,t) = R - \sum_{j=2}^{N+1} a_j c_B(x_j,t) \tag{32}$$

where

$$Q = \frac{1}{A_{1,1}}\left[\frac{i\tau^{\frac{1}{2}}}{nFA[A^\circ]D^{\frac{1}{2}}\beta^{\frac{1}{2}}} - A_{1,N+2}\right] , \tag{33}$$

$$R = \frac{1}{A_{1,1}}\left[\frac{i\tau^{\frac{1}{2}}}{nFA[A^\circ]D^{\frac{1}{2}}\beta^{\frac{1}{2}}}\right] , \quad \text{and} \tag{34}$$

$$a_j = \frac{A_{1,j}}{A_{1,1}} \tag{35}$$

Substitution of (31) and (32) back into (25) and (26), we have

$$\frac{dc_A}{dt} = S_j + \beta \sum_{j=2}^{N+1} b_{i,j} c_A(x_j,t) \quad , \quad \text{and} \tag{36}$$

$$\frac{dc_B}{dt} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_B(x_j, t) \quad , \quad \text{where} \tag{37}$$

$$S_i = \beta [B_{i,1} Q + B_{i,N+2}] \quad , \tag{38}$$

$$T_i = \beta B_{i,1} R \quad , \text{ and} \tag{39}$$

$$b_{i,j} = -B_{i,1} a_j + B_{i,j} \tag{40}$$

Simultaneous solution of the 2N differential equations by the integration subroutines described previously give accurate and fast approximations to the consentration profiles of A and B as a function of time.

The desired response, potential as a function of time, is given then by equation (11) in the form

$$E = E^\circ - \frac{RT'}{nF} \ln \left(\frac{c_B(0,t)}{c_A(o,t)} \right) \quad , \tag{41}$$

with $c_B(0,t)$ and $c_A(0,t)$ being supplied at each time integration step by equations (31) and (32). A comparison of some typical E-t points from equation (2) and from equation (41) is given in Table 1, and the simulated plot shown in Figure 1. Only a sixth order Legendre polynomial (N = 6) was used. Total computational time for 1000 E-t points was 0.862 seconds (see Computational section). β may either be determined explicitly[7], or fixed arbitrarily and integrated by splines[2].

EC$_{rev}$ Mechanism

The extension of the mathematics to include kinetic reactions

is immediate. Consider (under the same experimental conditions) the EC_{rev} mechanism:

$$A \underset{}{\overset{ne^-}{\rightleftharpoons}} B$$

$$(42)$$

$$B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$
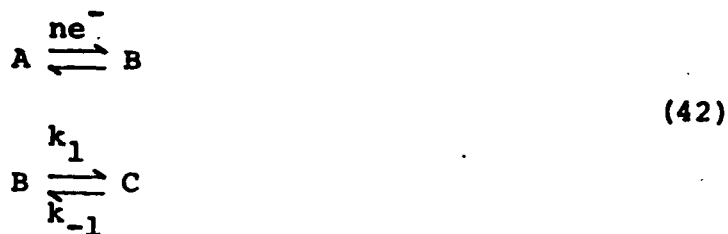
with
$$K = \frac{k_{-1}}{k_1} \quad , \quad \text{and} \tag{43}$$

$$\lambda = (k_1 + k_{-1})\tau \tag{44}$$

The diffusion-kinetic equations and boundary conditions describing the system are:

$$\frac{\delta[A]}{\delta T} = D_A \frac{\delta^2[A]}{\delta X^2} \tag{45}$$

$$\frac{\delta[B]}{\delta T} = D_B \frac{\delta^2[B]}{\delta X^2} - k_1[B] + k_{-1}[C] \tag{46}$$

$$\frac{\delta[C]}{\delta T} = D_C \frac{\delta^2[C]}{\delta X^2} + k_1[B] - k_{-1}[C] \tag{47}$$

$$[A]_{X,0} = [A]_{\infty,T} = 0 \ [A^\circ] \tag{48}$$

$$[B]_{X,0} = [B]_{\infty,T} = 0 \tag{49}$$

$$[C]_{X,0} = [C]_{\infty,T} = 0 \tag{50}$$

$$D_A \left(\frac{\delta[A]}{\delta X}\right)_{X=0} = -D_B \left(\frac{\delta[B]}{\delta X}\right)_{X=0} \tag{51}$$

$$D_C \left(\frac{\delta [C]}{\delta X} \right)_{X=0} = 0 \qquad (52)$$

Introducing the dimensionless parameters for concentration, time, and distance, the following simplified equations are readily obtained:

$$\frac{\delta c_A}{\delta t} = \beta \frac{\delta^2 c_A}{\delta x^2} \qquad (53)$$

$$\frac{\delta c_B}{\delta t} = \beta \frac{\delta^2 c_B}{\delta x^2} - \lambda (1+K)^{-1} (c_B - K c_C) \qquad (54)$$

$$\frac{\delta c_C}{\delta t} = \beta \frac{\delta^2 c_C}{\delta x^2} + \lambda (1+K)^{-1} (c_B - K c_C) \qquad (55)$$

$$c_A(x,0) = c_A(1,t) = 1 \qquad (56)$$

$$c_B(x,0) = c_B(1,t) = 0 \qquad (57)$$

$$c_C(x,0) = c_C(1,t) = 0 \qquad (58)$$

$$\left(\frac{\delta c_A}{\delta x} \right)_{x_1=0} = -\left(\frac{\delta c_B}{\delta x} \right)_{x_1=0} \qquad (59)$$

$$\left(\frac{\delta c_C}{\delta x} \right)_{x_1=0} = 0 \qquad (60)$$

Equations (53)-(55) are discretized by equation (20) to yield, after partial expansion and substitution of boundary condition (56)-(58),

$$\frac{dc_A(t)}{dt} \bigg|_{x_i} = \beta [B_{i,1} c_A(0,t) + B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij} c_A(x_j,t)] \qquad (61)$$

$$\frac{dc_B(t)}{dt}\bigg|_{x_i} = \beta\,[B_{i,1}c_B(0,t) + \sum_{j=2}^{N+1} B_{i,j}c_B(x_j,t)] -$$

$$\lambda(1+K)^{-1}[\,c_B(x_i,t) - Kc_C(x_i,t)] \tag{62}$$

$$\frac{dc_C(t)}{dt}\bigg|_{x_i} = \beta\,[B_{i,1}c_C(0,t) + \sum_{j=2}^{N+1} B_{i,j}c_C(x_j,t)] +$$

$$\lambda(1+K)^{-1}[c_B(x_i,t) - Kc_C(x_i,t)] \tag{63}$$

The flux relation (59) is identical to the simple reversible charge transfer case, and is discretized in precisely the same manner to yield equations (31) and (32). The flux relation for species c is equation (60), and is discretized as

$$\left(\frac{\delta c_C}{\delta x}\right)_{x=0} = 0 = \sum_{j=1}^{N+2} A_{1,j}c_C(x_j,t) \tag{64}$$

$$= A_{1,1}c_C(0,t) + A_{1,N+2}c_C(1,t) + \sum_{j=2}^{N+1} A_{1,j}c_C(x_j,t) \tag{65}$$

$$= A_{1,1}c_C(0,t) + \sum_{j=2}^{N+1} A_{1,j}c_C(x_j,t) \tag{66}$$

or

$$c_C(0,t) = \sum_{j=2}^{N+1} a_j c_C(x_j,t) \tag{67}$$

Substitution of (31), (32) and (67) into (61), (62), and (63) gives

$$\frac{dc_A}{dt}\bigg|_{x_i} = S_j + \beta \sum_{j=2}^{N+1} b_{i,j}c_A(x_j,t) \tag{68}$$

$$\frac{dc_B}{dt}\bigg|_{x_i} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_B(x_j, t) - \lambda(1+K)^{-1}[\, c_B(x_i, t) - Kc_C(x_i, t)] \qquad (69)$$

$$\frac{dc_C}{dt}\bigg|_{x_i} = \beta \sum_{j=2}^{N+1} b_{i,j} c_C(x_j, t) + \lambda(1+K)^{-1}[c_B(x_i, t) - Kc_C(x_i, t)] \qquad (70)$$

Again, simultaneous solution of equations (68)-(70) provide the time dependent concentration profiles. The chronopotentiometric response for this mechanism is still given by equation (41) with the term in parentheses being supplied by equations (31) and (32). The concentration terms in (31) and (32) however, are now calculated numerically from equations (68)-(70).

The results of the simulation of this mechanism was compared to the response given by the analytic solution[6]

$$E = E^\circ - \frac{RT'}{nF}\ln\frac{T^{\frac{1}{2}}}{\tau^{\frac{1}{2}} - T^{\frac{1}{2}}} + \frac{RT'}{nF}\ln\left[\frac{1}{1+k} + \frac{\pi^{\frac{1}{2}}K}{2(1+K)}\frac{\mathrm{erf}[(k_1 + k_{-1})^{\frac{1}{2}}T^{\frac{1}{2}}]}{(k_1 + k_{-1})^{\frac{1}{2}}T^{\frac{1}{2}}}\right]^{-1} \qquad (71)$$

The comparison of the two solutions shows that the simulated results are easily maintained within a relative error of 0.01% when β is chosen by the method described by Rieker and Speiser[7].

Simulations for more complicated mechanisms are formulated simply by the same procedures used to arrive at equations (68)-(70). Under similar boundary conditions, the results are quite easily obtained.

Computational

All simulations were performed on the Amdahl 470V7 computer at the University of Alberta. The main integration subroutine for the system of coupled first order ordinary differential equations

((36)-(37) or (68)-(70)) was the same third order semi-implicit Runge-Kutta method as described previously[2] for "stiff" equations. The subroutine is very general in usage, and calls three external subroutines furnished by the user[8]: the first supplies the algorithm for the right hand side of the time derivatives of each concentration term (equations (36)-(37) or (68)-(70)), the second is a simple output routine for displaying the results and is called automatically, and the third is a user supplied matrix of the Jacobian of equations (36)-(37) or (68)-(69), necessary during the integration.

The elements of the Jacobian matrix are simply the derivatives of equations (36)-(37) or (68)-(70) with respect to each x_j. The matrix elements of the Jacobian for the simple reversible electron transfer mechanism then are given by:

$$J_{i,j} = \frac{\delta}{\delta x_j}\left(\frac{dc_A(t)}{dt}\right)\bigg|_{x_i} \qquad \text{for species A} \qquad (72)$$

and

$$J_{i,j} = \frac{\delta}{\delta x_j}\left(\frac{dc_B(t)}{dt}\right)\bigg|_{x_i} \qquad \text{for species B} \qquad (73)$$

These are given explicitly by:

$$J_{i,j} = \frac{\delta}{\delta x_j}\left(S_i + \sum_{j=2}^{N+1} b_{i,j}c_A(x_j,t)\right) \qquad (74)$$

for species A, and

$$J_{i,j} = \frac{\delta}{\delta x_j}\left(T_i + \sum_{j=2}^{N+1} b_{i,j}c_B(x_j,t)\right) \qquad (75)$$

for species B, or finally,

$$J_{i,j} = b_{i,j} = \frac{-B_{i,1}A_{1,j}}{A_{1,1}} + B_{i,j} \qquad (76)$$

for both species.

Similarily, the matrix elements of the Jacobian for the EC_{rev} mechanism are given by:

$$J_{i,j} = \text{equation (76)} \qquad (77)$$

for species A, and

$$J_{i,j} = \frac{-B_{i,1}A_{1,j}}{A_{1,1}} + B_{i,j} - \lambda K(1+K)^{-1} c_B(x_i,t)\delta_{ij} \qquad (78)$$

for species B, where δ_{ij} is the Kronecker delta, and

$$J_{i,j} = \frac{-B_{i,1}A_{1,j}}{A_{1,1}} + B_{i,j} - \lambda K(1+K)^{-1} c_C(x_i,t)\delta_{ij} \qquad (79)$$

for species C.

Acknowledgements

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Table 1

Time/s	E/volts, simulated	E/volts exact
0.0023	0.0771	0.0771
0.0107	0.0556	0.0556
0.0418	0.0351	0.0351
0.1188	0.0167	0.0167
0.3358	-0.0048	-0.0048
0.5055	-0.0227	-0.0227
0.9100	-0.0752	-0.0752
0.9940	-0.1241	-0.1240

Comparison of simulated results with exact (equation 2) for simple reversible charge transfer. $i = 0.269$ ma, $\tau = 1.010$ s, $D = 10^{-5}$ cm^2/sec, $[A°] = 1 \times 10^{-6}$ mole/cm^3, $T = 25°C$, $A = 1.000$ cm^2, linear diffusion, quiet solution, $E° = 0.000$ V.

Figure 1: Calcomp digital plot of simulated chronopotentiogram

for simple reversible charge transfer mechanism. See

Table 1 for experimental parameters.

Appendix

Listed below are the discretized equations for several other commonly occurring electrochemical mechanisms. As above, it is assumed that the diffusion is to a planar electrode in quiet solution, and species A is the only electroactive species present initially.
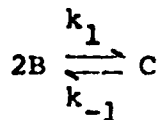
Catalytic Mechanism

$$A \underset{\longleftarrow}{\overset{ne^-}{\longrightarrow}} B \overset{k}{\longrightarrow} A + C \tag{80}$$

$$\frac{dc_A}{dt}\Bigg|_{x_i} = S_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_B(x_j,t) - k\tau c_B(x_j,t) \tag{81}$$

$$\frac{dc_B}{dt}\Bigg|_{x_i} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_B(x_j,t) - k\tau c_B(x_j,t) \tag{82}$$

For the E-t profile, equation (11) is used along with equations (31) and (32), the unknown concentration terms being furnished by the simultaneous solution of the 2N equations (81) and (82).

Dimerization

$$A \underset{\longleftarrow}{\overset{ne^-}{\longrightarrow}} B$$

$$\tag{83}$$

$$2B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

We let

$$\lambda = ([A°]k_1 + k_{-1})\tau, \text{ and} \tag{84}$$

$$K = \frac{k_{-1}}{[A°]k_1} \tag{85}$$

Then
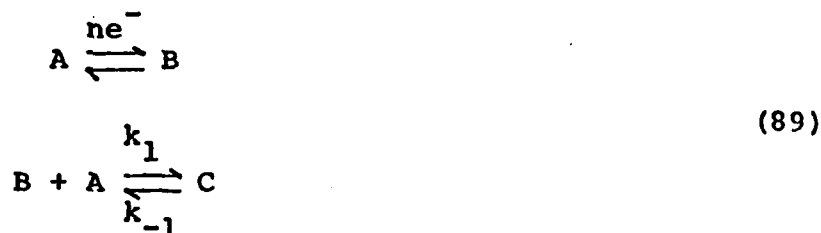
$$\frac{dc_A}{dt} = S_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_A(x_j,t) \tag{86}$$

$$\frac{dc_B}{dt} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_B(x_j,t) - \lambda(1+K)^{-1}(c_B(x_i,t)^2 - Kc_C(x_i,t)) \tag{87}$$

$$\frac{dc_C}{dt} = \beta \sum_{j=2}^{N+1} b_{i,j} c_C(x_j,t) + \lambda(1+K)^{-1}(\tfrac{1}{2}c_B(x_i,t)^2 - Kc_C(x_i,t)) \tag{88}$$

Once more, equations (11), (31), and (32) are used for the E-t profiles. Note that in this case, 3N equations must be solved because $c_B(0,t)$ depends on the concentration of the C species.

<u>Second Order Reaction</u>
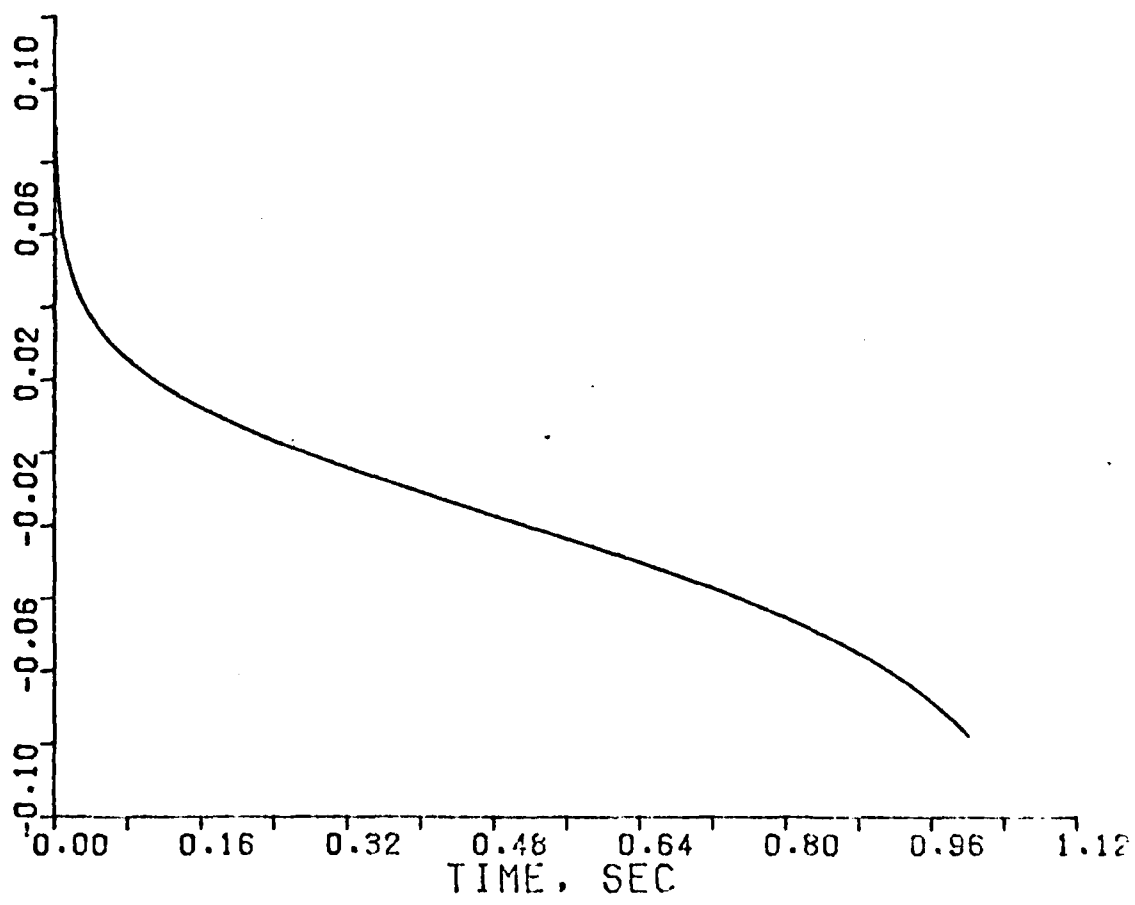
$$A \underset{}{\overset{ne^-}{\rightleftharpoons}} B$$

$$B + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \tag{89}$$

λ and K are defined as in equations (84) and (85).

$$\frac{dc_A}{dt} = S_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_A(x_j,t) - \lambda(1+K)^{-1}(c_A(x_i,t)c_B(x_i,t) -$$

$$Kc_C(x_i,t)) \tag{90}$$

$$\frac{dc_B}{dt} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_B(x_j,t) - \lambda(1+K)^{-1}(c_A(x_i,t)c_B(x_i,t) -$$

$$Kc_C(x_i,t)) \tag{91}$$

$$\frac{dc_C}{dt} = \beta \sum_{j=2}^{N+1} b_{i,j} c_C(x_j, t) + \lambda(1+K)^{-1}(c_A(x_i, t)c_B(x_i, t) - Kc_C(x_i, t)) \qquad (92)$$

TIME, SEC